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## OFFICE OF NAVAL RESEARCH Contract N00014-75-C-0730

TECHNICAL REPORT No.8

THE OXIDATION OF CARBIDIC MONOLAYERS ON Ni(110)

by

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January 15, 1980

Preprint of a Paper Submitted to Surface Science

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### **ABSTRACT**

Previous studies of ethylene adsorption and decomposition on a Ni(110) single crystal surface have been extended to measurement of the interaction of oxygen molecular beams with the carbonaceous layers formed in the ethylene adsorption process. A combination of Auger electron spectrometric and modulated molecular beam techniques have been used to measure the kinetics of oxygen adsorption and CO production on the surface. Results for oxygen adsorption on the clean Ni(110) surface are in agreement with previous studies. For the surface formed by adsorbing ethylene on the clean nickel surface at room temperature, room temperature adsorption of oxygen results in formation of a surface layer of NiO without removal of carbon from the surface. Heating the layer formed at room temperature above 500K leads to a surface rearrangement that produces two different surface carbon species both of which react with oxygen to form CO. The kinetics of the oxidation of one species can be described in terms of partial control by the surface oxidation process and partial control by desorption of product. Competing carbon dissolution and nickel oxide forming processes preclude quantitative evaluation of the oxidation kinetics of the other carbon species.

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#### 1. INTRODUCTION

In a previous paper (1) we described the adsorption and decomposition of ethylene on a clean Ni(110) surface over a wide range of temperatures. At all temperatures studied, the reaction proceeded by dissociative adsorption of the ethylene, with complete dehydrogenation, and desorption of the resulting hydrogen molecules into the gas phase. The surface carbon concentration resulting from this adsorption process was dependent on the temperature at which the adsorption took place. For temperatures below 620K, the final coverage corresponded to one carbon atom per surface nickel atom, probably representing a dehydrogenated C2 molecular surface species. For temperatures between 620K and 800K, the final coverage corresponded to a monolayer of carbon having an interatomic spacing the same as the C-face of graphite. At higher temperatures no residual carbon was observed on the surface, indicating dissolution into the bulk of the nickel crystal.

We have extended the above study to an investigation of the interaction of these carbonaceous adlayers with gaseous oxygen. This is a reaction that is of interest for at least two reasons. First, it was observed in the previous study that a molecularly adsorbed phase of ethylene was formed on the surface following formation of the dissociatively adsorbed layer at T<620K. Possible reactivity of this phase with oxygen would be indicated if this surface proved action for the dissociative adsorption of oxygen. Second, the graphitic layer formed at higher temperatures appeared to be inert to further adsorption, and may represent a "poisoned" state of the catalyst surface. If this is so, then reaction of this carbon with gaseous oxygen would provide a mechanism for regeneration of the clean surface. With this in mind, we have observed the kinetics of the overall reaction

$$g^{0}2 + a^{C} + g^{C}0 \tag{1}$$

over a range of surface temperatures and initial surface carbon concentrations, using Auger electron spectrometry (AES) to measure surface carbon and oxygen concentrations, and a combination of dc mass spectrometric detection and molecular beam relaxation spectroscopy (MBRS) to measure scattered oxygen and product CO signal phase and amplitude. In the present report we discuss the results obtained at T< 600K. The results for T> 600K will be presented separately.

#### EXPERIMENTAL

The measurements were carried out in the surface research system used for the previous studies, and described in detail in the report of that work. In brief, it consists of a large metal ultrahigh vacuum chamber. The surface under study is mounted on the axis of the chamber using a universal positioning device. The reactant beam is formed by a supersonic nozzle source in a differentially-pumped auxiliary chamber, and modulated in a second differentially-pumped chamber before it enters the main reaction chamber. The main chamber also contains the mass spectrometer used to detect the scattered product signal, a cylindrical mirror Auger electron spectrometer, and an ion gun for surface cleaning between experimental runs.

Two modifications have been made to this system since the previous study. The detector mass spectrometer has been fitted with a new ion source, which has resulted in an improvement of the signal-to-noise ratio of the detector by about a factor of five. The original beam modulation system, a large, multi-toothed chopper wheel driven by a motor external to the vacuum system, has been replaced by a much smaller wheel, driven by a motor inside the collimator chamber. Installation of this sytem has increased the available modulation frequency range to 15-300 Hz. In the present work the mass spectrometer detector output was sensed by a Princeton Applied Research

Model 2504 two-phase lock-in amplifier. This unit permits simultaneous measurement of product signal phase and amplitude, and has proven invaluable in following the rapidly-changing CO product signal phase observed during the surface oxidation reaction at high temperatures.

The sample used in this study was the same one used in the previous work. A nickel single crystal 2.5 cm long, 0.6 cm wide and 0.025 cm thick, with a (110) orientation on the flat surface. It was cleaned prior to the experimental studies and between runs by cycles of argon ion bombardment followed by anneal at 800K, until the Auger spectrum of the crystal showed only those peaks typical of the clean nickel surface. In this phase of the work, carbonaceous layers were formed on the nickel surface by exposure to an ethylene molecular beam at temperatures close to ambient until saturation of the carbon AES signal was observed.

This process was observed in the previous work to lead to decomposition of the ethylene, with desorption of the hydrogen as H<sub>2</sub> and formation of an adlayer structure having one carbon atom per surface nickel atom (1.1x10<sup>15</sup> carbon atom/cm<sup>2</sup>). The carbon AES peak associated with this structure had the typical "graphitic" shape. Annealing this adlayer phase at temperatures above 525K resulted in change in the AES peak shape to a typically "carbidic" shape and, as we shall see later, formation of two carbon species on the surface that differ markedly in their reactivity with oxygen, both from each other and from the species formed by ethylene deposited at ambient temperatures. We will thus report separately the results obtained for the as deposited layer and the annealed layer.

Two techniques were used to follow surface reaction kinetics for all experimental conditions studied. Auger spectroscopy was used to monitor surface carbon and oxygen concentrations as exposure to ethylene or oxygen took place. Previous studies have indicated that in this case the presence

of the Auger primary electron beam does not observably affect the kinetics of the surface processes involved. The flux of molecules from the surface during the reaction process was measured mass spectrometrically, using a modulated reactant beam and either the two-phase lock-in amplifier at the mass spectrometer output to obtain information on both the magnitude and phase of the scattered reactant and product species signals or simple dc detection of the product flux from the surface, in the case of slow surface processes.

#### 3. RESULTS

#### Oxygen Adsorption on Clean Nickel

The initial measurement made was of the rate of oxygen adsorption on the clean Ni(110) surface. The sticking coefficient for this process, obtained from analysis of the oxygen mass spectrometer signal observed for oxygen beam scattering from an initially clean surface, shown in Figure 1, is  $S_0 = 0.78$ . The overall uptake rate, as obtained by measurement of the oxygen AES signal from the nickel surface as a function of oxygen exposure is shown in Figure 2. The initial process is characterized by the dissociative adsorption of oxygen, with a sticking coefficient

$$S = S_0 (1-0)$$

where  $\theta$  is the fractional oxygen adatom coverage.  $\theta=1$  at an oxygen coverage of  $\sim 5.5 \times 10^{14}$  atom/cm<sup>2</sup>. The further increase in oxygen AES beyond this point is attributed to the formation of a surface layer of NiO. The saturation oxygen coverage for this process was found to be  $2.4 \times 10^{15}$  atom/cm<sup>2</sup>, which corresponds to 3 monolayers of NiO on the (110) surface. These results, and this interpretation, are in agreement both with previous studies in this laboratory of oxygen adsorption on Ni(111) and Ni(100)<sup>(2)</sup> and the results of Norton et al. on Ni(110), Ni(111) and Ni(100)<sup>(3)</sup>

## Oxygen Reaction with the as-deposited carbon layer at 300K.

Mass spectrometric measurement of oxygen scattering from the surface formed by exposure of the clean nickel surface to ethylene at room temperature, as shown in Figure 1, indicated an initial sticking coefficient for oxygen adsorption of  $\sim 0.2$ . The rate of surface oxygen buildup, and the accompanying decrease in the carbon AES signal, are shown in Figure 3. For this case, the oxygen adsorption kinetic curve is very similar to that observed for the clean surface case, differing primarily in the absolute rate, due to the lower initial sticking coefficient. In both of these cases, there is an inflection point in the uptake curve at ~6x1014 atom/cm2. where NiO formation takes over from the oxygen chemisorption process. The saturation oxygen coverage is similar for both surfaces. The decrease in the carbon AES signal follows the increase in the oxygen signal closely. This can be seen in Figure 4, where we compare the attenuation of the carbon AES signal at various oxygen coverages with the oxygen AES signal multiplied by 0.433, a figure chosen to make the two curves coincide at the highest oxygen exposures measured. This behavior is what one would expect if the decrease in the carbon AES signal were due solely to scattering of the Auger electrons produced by a constant concentration of carbon atoms by an increasingly thick adlayer of oxygen or NiO. The only departure observed from this behavior is at the point in the process where the NiO layer is first forming and presumably growing to consume the oxygen adlayer.

A layer of NiO three monolayers thick would have a thickness of 4.43A. (3)

The observed attenuation factor of 0.433 for this layer is consistent with an escape depth of ~8Å for the 273 eV carbon Auger electrons. This figure is in good agreement with measurements made in other studies. (4) The fact that the carbon signal is significantly attenuated even at low oxygen coverages suggests

that the carbon atom adsorption sites lie very close to the nickel surface, possibly even within the outermost layer of the surface.

Oxygen Reaction with the Adlayer Structure Formed by Heating to 525K.

As was mentioned earlier, heating the carbon layer formed by  $\mathrm{C_{2}H_{4}}$  adsorption at room temperature to temperatures above 525K resulted in a surface reaction leading to the formation of two different carbon species on the surface. The evidence for this reaction is, first, the observed change in the carbon AES peak that occured as the reaction took place and, second, the observed change in the reactivity of the carbon layer with oxygen, both at high temperatures and at room temperature.

In our attempt to characterize the kinetics of the oxidation of this carbon adlayer, we have studied both the oxidation process itself and the adsorption and desorption kinetics of CO on both the clean and carbon-covered nickel surface. We shall see later that both types of data are required for complete characterization of the surface reaction process.

We have observed the reaction of oxygen gas with the layer formed in the heating process over the temperature range from 300 to 600K, using both AES and mass spectrometric detection. The AES measurements of surface oxygen and carbon concentrations for this case were qualitatively similar to those observed for oxygen adsorption on the unannealed layer at room temperature. They differ quantitatively however, in that the rate of increase in the chemisorbed oxygen signal is significantly greater than for the unannealed layer, and the rate of decrease in the surface carbon signal is much greater than the previous case. This latter effect is due to the fact that carbon is being removed from the surface as CO, rather than just being subjected to Auger signal attenuation by oxygen adsorption. The increased oxygen adsorption rate is most probably due to the increasing availability of sites for oxygen dissociation due to the removal of carbon by the oxidation reaction. This increased rate of oxygen uptake is also evident in the mass spectrometric

measurement of scattered oxygen flux for this case, shown in Figure 1.

Over the entire temperature range studied, CO evolution was observed by d.c. mass spectrometric detection when oxygen struck the surface. At temperatures of 525K and above, an a.c. mass spectrometer signal for CO was also observed. The results of the d.c. measurements are shown in Figure 5. Graphical integration of the area under the curves, using the measured mass spectrometer sensitivity for CO, indicates that at temperatures at or below 475K, the total amount of carbon removed is approximately 2x1014 atom/cm2. Measurements of the a.c. mass spectrometer signal phase and amplitude for CO, taken during the reaction at 535K, are shown in Figure 6. They also indicate a rapid removal of a fraction of the surface carbon as CO. Again the amount consumed in this reaction is approximately 2x10<sup>14</sup> atom/cm<sup>2</sup>. The carbon removed in this fast reaction corresponds within experimental error to 20% of the carbon in the as-deposited layer. It is thus apparent that 80% of the carbon originally deposited is in some other surface structure. For the present we will refer to these two distinct carbon species as "excess" and carbidic" for the 20% and 80% fractions respectively.

The observed signal vs. time curve for the a.c. detection at 535K, taken at an oxygen flux  $9 \times 10^{13} \text{molec/cm}^2 \text{sec}$ , fits a first-order kinetic curve with an apparent first-order rate constant  $K = 0.074 \text{ sec}^{-1}$ . The form of the d.c. CO evolution curves at lower temperatures is more complicated, showing an initial rise, followed by a more-or-less exponential decay. Curves of this form are typical of reaction schemes involving consecutive reaction steps. (5) It will be shown later that these data are well described by such a sequence, involving surface CO production followed by CO desorption. Additional measurements at 535K indicated that the overall rate of this oxidation process is also first-order in the oxygen flux to the surface.

The oxidation of the "carbidic" fraction of the surface carbon is considerably slower than that of the "excess" carbon. It can be seen from Figure 5 that the reaction rate increases with increasing temperature, but in the higher temperature ranges, where one might expect to obtain kinetic information from a.c. detection of evolved CO, there is serious competition between CO formation and dissolution of adsorbed carbon.

We have also observed the rate of the slower oxidation reaction as a function of time after the oxygen beam was shut off. The rate decreased exponentially with time, with a first-order rate constant K = 0.132 sec<sup>-1</sup> for an initial oxygen flux of  $1 \times 10^{14} \text{molec/cm}^2 \text{sec}$  and a surface temperature of 535K. This is long compared to the time required for the system pumping system to reduce the pressure after oxygen shutoff. The observed rate constant is, however, consistent with that expected for CO desorption from clean nickel at the temperature of experiment. Only a small fraction of the carbon and oxygen on the surface at shutoff was removed in this final transient. Thus it appears that strongly chemisorbed oxygen is inactive in the oxidation process, no reaction between this species and the surface carbon being observed after the oxygen molecular beam was shut off.

The adsorption-desorption kinetics of CO on both the clean and carbon-covered nickel surfaces were measured using molecular beam relaxation spectroscopy. The amplitude of the a.c. signal arising from the scattering of a CO molecular beam from the sample surface is shown in Figure 7 for the two cases studied. An equation for the desorption rate constant vs. temperature can be extracted from data of this type using the equations (6)

$$\varepsilon = \frac{1}{(1 - (\omega/K_D)^2)^{1/2}} \tag{2}$$

in which  $\epsilon$  is the a.c. signal amplitude relative to the amplitude at high temperature,  $\omega$  the modulation frequency and  $K_D$  the desorption rate constant, and the Arrhenius relation for  $K_D$ ,

$$K_{D} = K_{D}^{\circ} e^{-\frac{\Delta H_{D}}{RT}}, \qquad (3)$$

in which  $\Delta H_{D}$  is the activation energy for desorption. Application of these relations to the data of Figure 7 yields

$$K_D = 6 \times 10^{14} \exp(\frac{-30500}{R_T})$$
 (4)

for the clean-surface case and

$$K_D = 4.0 \times 10^6 \exp(\frac{-11600}{R_T})$$
 (5)

for the surface covered with the carbon adlayer. The value for the clean surface case is in good agreement with the result of a similar measurement by Helms and Madix, (7) namely

$$K_D = 2 \times 10^{15} \exp(-\frac{33000}{R_T})$$
 (6)

The result for the carbon-covered surface indicates that CO is bound much more weakly to this surface.

#### 4. DISCUSSION

#### Oxygen on Clean Ni(110)

The reaction of oxygen gas with various nickel surfaces is perhaps the most studied system in recent years. In addition to the previously mentioned adsorption studies (2,3) this system has been studied extensively by low energy electron diffraction (8) and reflection high energy electron diffraction. (9) The sequence invariably observed is the dissociative adsorption of oxygen to form an ordered chemisorbed structure, followed by the nucleation and growth of a layer of NiO, generally found to be three monolayers of NiO in thickness. The results presented here do not add significantly to our understanding of this system. On the contrary, the agreement with previous studies is taken as evidence of the proper functioning and calibration of the present experimental system. Consequently no more will be said about this phase of the study.

## Oxygen on the As-Deposited Carbon Layer at 300K

The apparent decrease in carbon coverage with increasing oxygen coverage in this case can be adequately accounted for in terms of attenuation of the AES signal from a constant surface carbon population by an increasingly thick oxygen or oxide overlayer. The only major effect that the presence of the adsorbed carbon appears to have on the oxygen adsorption process is a reduction in the sticking coefficient for the dissociative adsorption process.

As was shown in Figure 4, the attenuation of the carbon AES signal caused by the oxygen adsorption process appears to be directly proportional to the surface oxygen coverage, except for a discrepancy at oxygen coverages between  $4 \times 10^{14}$  and  $1.2 \times 10^{15}$  atom/cm<sup>2</sup>. This is the coverage region in which the NiO layer is nucleated and begins to grow. The surface rearrangements involved in this process may account for the irregularity in the carbon AES attenuation. This proportionality between oxygen coverage and AES attenuation, even at low oxygen coverage, is strong evidence that the carbon adsorption sites lie closer to the nickel surface than the adsorbed oxygen atoms do, and that as the NiO layer grows, the carbon layer remains at the interface between the nickel and NiO phases. Further evidence for this position comes from the agreement between the escape depth for carbon Auger electrons calculated from this work, assuming a NiO layer three monolayers thick, and the value determined experimentally by others. (4)

#### The Carbon Surface Rearrangement at 525K

The results obtained during oxygen exposure of the carbon layer formed by heating the as-deposited layer above 525K are the most interesting, as the species produced in the formation of this layer are the only ones that react with gaseous oxygen in the temperature range covered in this work. Consider first the nature of the surface reaction in the carbon adlayer. Auger spectra taken during this reaction showed a change in carbon peak shape from a typical

"graphitic", or hydrocarbon shape to a typical "carbidic" shape. Oxidation kinetic measurements indicate that roughly 20% of the carbon initially present on the surface is converted to the species that reacts rapidly with oxygen, while the remainder is converted to the slowly-reacting species. LEED studies of carbon layers by others have shown a variety of structures. Of interest here are the 2xl structure observed by Pitkethly (10) after exposure to acetylene and the 4x5 structure observed by Pitkethly after heating the layer described above and by Schouten et al. (11) after dosing the surface with methane. All of the above results are consistent with a reaction sequence involving dehydrogenation of ethylene or acetylene without breakage of the C-C bond and with formation of the (2x1) ordered structure of surface C, molecules at room temperature, followed by breakage of the C-C bond and surface rearrangement to form the (4x5) surface structure, plus some second surface carbon species, represented by the "excess" carbon observed in the present work. In the work of Schouten et al., where the dosing gas was methane, the (4x5) structure was formed directly, as no C-C bond breaking is required in this case.

### Kinetics of the Reaction of Oxygen with the Annealed Layer

Assuming the above interpretation to be correct, it remains to explain the observed kinetics of the reactions of these two carbon species with oxygen. The reaction sequence is complicated, as several surface reactions are going on concurrently and, under the conditions of this study, none of the reactions proceeds at steady state.

In the case of the fast reaction, the available data are sufficient for a detailed description of the reaction process. It was observed that the surface reaction proceeded only when the surface was exposed to gaseous oxygen; strongly chemisorbed oxygen was observed not to play a role in the reaction sequence. One can thus describe the reaction sequence formally as

$$g_{2} \stackrel{?}{\leftarrow} a_{x}$$
 (7)

$${}_{a}^{0} {}_{x} + {}_{x}^{C} + {}_{a}^{CO}$$
 (8)

$$a^{CO} \rightarrow g^{CO}$$
 (9)

in which  $_{a}^{0}$  is a reactive oxygen surface species and  $_{x}^{0}$ C represents the adsorbed "excess" carbon. The fact that the reaction rate is first-order in the oxygen flux to the surface indicates that reaction 7 goes to equilibrium very quickly. The observed form of the d.c. CO evolution curves, especially at low temperatures, suggests that the overall CO production rate is controlled by the consecutive reactions 8 and 9. For a given oxygen flux and surface temperature, assuming reaction 7 to be fast and reversible, we can treat the overall process as consisting of two consecutive first-order reactions. The rate of reaction 8 is given by

$$\frac{d \left[a^{CO}\right]}{dt} = K_1 \left[x^{C}\right], \tag{10}$$

in which  $K_1 = K_1' \begin{bmatrix} 0 \\ a'x \end{bmatrix}$ , with  $\begin{bmatrix} 0 \\ a'x \end{bmatrix}$  assumed constant for a given oxygen flux and temperature. The rate of reaction 9 is given by

$$\frac{d[_aCO]}{dt} = K_2 [_aCO]$$
 (11)

The observed gaseous CO flux is directly proportional to the rate of reaction. (9) The overall rate of this consecutive reaction sequence is given in standard references on chemical kinetics (5) as

$$\frac{d[g^{CO}]}{dt} = \frac{-d[a^{CO}]}{dt} = K_2[a^{CO}] = \frac{[x^C]_0}{\frac{1}{K_1} + \frac{1}{K_2}} (e^{K_1 t} - e^{-K_2 t}) \quad (12)$$

in which  $[{}_{\mathbf{x}}^{\mathbf{C}}]_{\mathbf{0}}$  is the concentration of "excess" carbon at time zero. We

have used this equation to fit both the d.c. data at 333, 363, 423 and 473K, and the a.c. data at 533K, making the following assumptions:

- 1. The constant  $K_2$  is equal to the desorption rate constant  $K_D = 4.0 \times 10^6 \exp{(-\frac{11600}{RT})}$  (5) found experimentally for the desorption of CO from the carbon-covered surface.
- 2. The constant K<sub>1</sub> is equal to the observed first-order rate constant determined in the a.c. measurement for the reaction at 533K°, where K<sub>2</sub> is very large, and varies exponentially with temperature.

The best fit to the complete set of data was obtained using the relation  $K_1 = 1.2 \times 10^{-2} \exp{(\frac{1950}{RT})}.$ (13)

An example of the fit obtained is given in Figure 8 where we compare the data obtained at 363K with the prediction of Equation 12, using  $K_1 = 0.17$ ,  $K_2 = 0.340$ . Considering the approximations involved and the complexity of Equation 12, the observed fit is considered to be very good. The fit to the data at other temperatures was comparable, and could be made even better in some cases by assuming errors in temperature measurement of ten degrees or less.

The rate of the fast reaction is thus seen to be well described by the consecutive reaction scheme. The apparent activation energy for the surface reaction step, embodied in  $K_1$ , is negative. This is consistent with the hypothesis that a loosely-bound oxygen species is involved in the reaction, as the pseudo-first-order rate constant  $K_1$  contains the surface concentration of this species. At a constant oxygen flux to the surface, this concentration would decrease exponentially with temperature, at a rate controlled by the heat of desorption of the species. Since typical values

for heats of desorption of physisorbed or weakly chemisorbed species cover the range from 4 to 10 Kcal/mol, this implies that the actual activation energy for the surface reaction step is in the range of 2 to 8 Kcal/mol.

The observed rate of the slower oxidation process, which contributes the bulk of the d.c. CO signal at temperatures above 525K, cannot be fit to any relatively simple set of rate equations. The rate of this reaction is slow enough that the bulk of the reaction takes place on a surface that has a high coverage of chemisorbed oxygen and eventually nickel oxide. Independent measurements of the rate of carbon dissolution into the crystal (12) indicate that the rate of this process is also significant at these higher temperatures. The only quantitative rate constant information obtained under these conditions was that for the desorption of product CO after the oxygen flux had been turned off. This rate, as mentioned earlier, was consistent with the expected desorption-rate for CO from clean nickel. Qualitatively, the rate of the slow reaction increased with increasing temperature, indicating a significant activation barrier for the COformation step. Again, we assume that since chemisorbed oxygen was observed to be inactive in the oxidation process, a precursor oxygen species is also involved in this reaction.

#### 5. CONCLUSION

The multiplicity of surface processes occuring on the carbon-covered nickel surface leads to overall surface reaction kinetics too complicated to be analyzed in complete detail. In spite of this complexity it is possible, using the multiple techniques available in the experimental system, to sort out the details of many of the unit processes involved. Definitive results of the present study are:

 Measurements of oxygen uptake on the clean nickel surface are in quantitative agreement with previous studies.

- Adsorption of ethylene on the clean nickel surface at room temperature leads to formation of a dehydrogenated carbon species, probably C<sub>2</sub> molecules. Saturation coverage is one carbon atom per surface nickel atom.
- 3. Annealing of this layer at T<535K leads to formation of an adlayer containing two distinct carbon species. The resulting "carbidic" shape of the carbon AES peak and the fact that 80% of the initial carbon layer is present as one of these species suggests that this is the (4x5) carbon on Ni(110) structure observed by others. The remaining 20% ("excess" carbon) is present on the surface as some other, more reactive species.
- 4. The layer formed at room temperature does not react with gaseous oxygen or chemisorbed oxygen. Oxygen exposure of this surface leads to oxygen chemisorption and oxide formation without disturbing the carbon layer.
- 5. Oxygen interaction with the layer formed by annealing the initial carbon deposit above 535K leads to oxidation of both surface carbon species present. The "excess" carbon is oxidized at all temperatures studied. Overall kinetics of this reaction are described by consecutive first-order oxidation and desorption processes. Detailed kinetic equations for the oxidation of the "carbidic" carbon could not be obtained due to interference from competing surface processes.
- 6. CO adsorption-desorption kinetic measurements on the clean surface yielded results in agreement with previous studies. Similar measurements on the carbon-covered surface indicated much weaker binding to this surface.

#### ACKNOWLEDGEMENT

This research was supported in part by the Office of Naval Research

under Contract No. N00014-75-C-0730. Their continuing support is grate-fully acknowledged. The assistance of Edward Kurz in the analysis of the data for the fast surface reaction is greatly appreciated.

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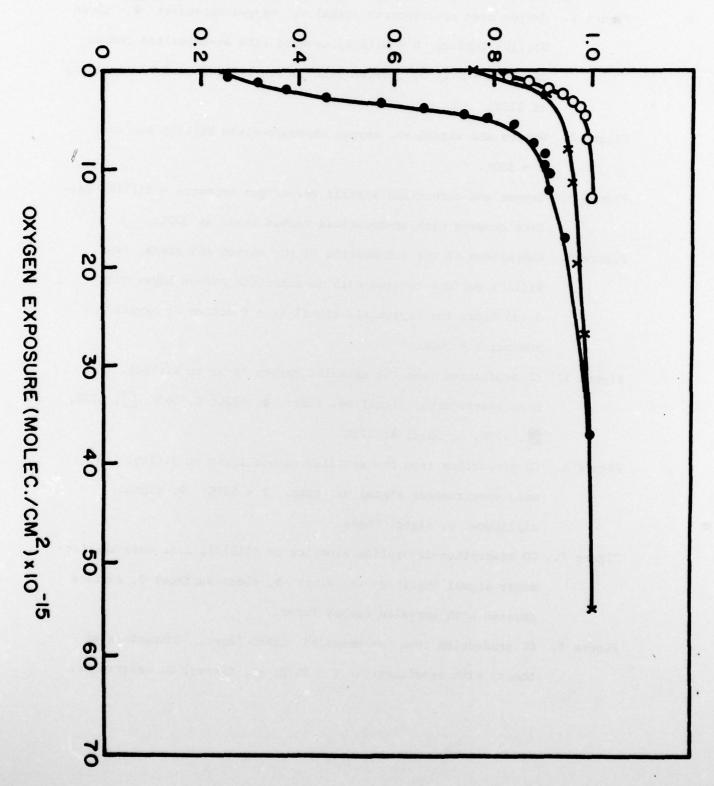
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#### FIGURE CAPTIONS

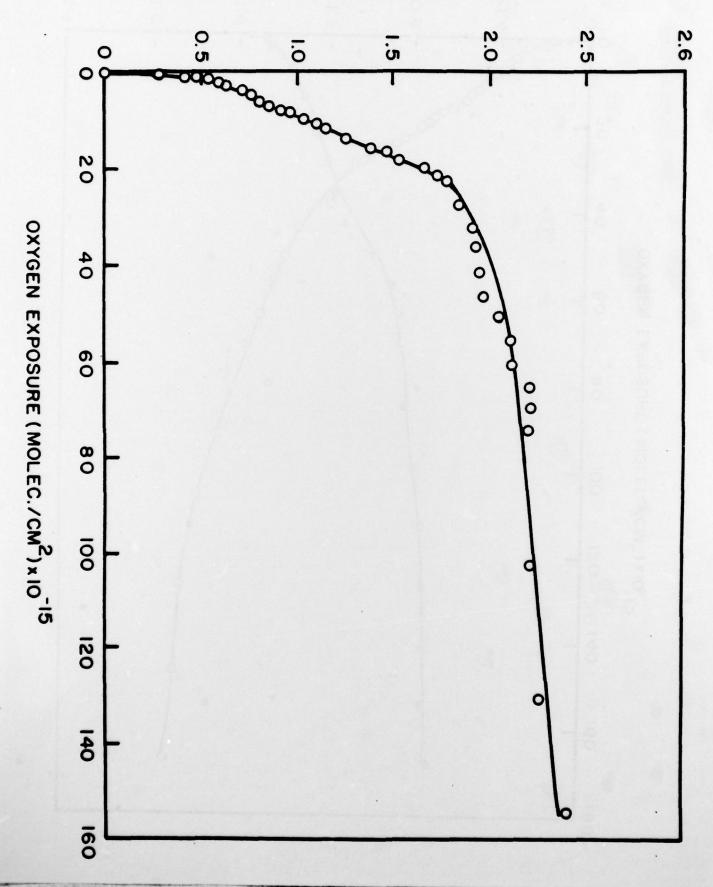
- Figure 1. Oxygen mass spectrometer signal vs. oxygen exposure: - clean Ni(110) surface; 0 Ni(110) covered with as-deposited carbon layer; X Ni(110) covered with carbon layer formed by annealing at 525K.
- Figure 2. Oxygen AES signal vs. oxygen exposure-clean Ni(110) surface;

  T = 300K.
- Figure 3. Oxygen and carbon AES signals vs. oxygen exposure Ni(110) surface covered with as-deposited carbon layer at 300K.
- Figure 4. Comparison of the attenuation of the carbon AES signal from Ni(110) surface covered with as-deposited carbon layer with 0.433 times the oxygen AES signal as a function of oxygen exposure; T = 300K.
- Figure 5. CO production from the annealed carbon layer on Ni(110). d.c. mass spectrometer signal vs. time: •, 333K; 0, 363K; □, 423K; □, 473K; Δ, 533K; Δ, 573K.
- Figure 6. CO production from the annealed carbon layer on Ni(110). a.c. mass spectrometer signal vs. time. T = 533K: •, signal amplitude; O, signal phase.
- Figure 7. CO adsorption-desorption kinetics on Ni(110), a.c. mass spectrometer signal amplitude vs. time: •, clean surface; 0, surface covered with annealed carbon layer.
- Figure 8. CO production from the annealed carbon layer. Comparison of theory with experiment at T = 363K: -, theory; O, experiment.

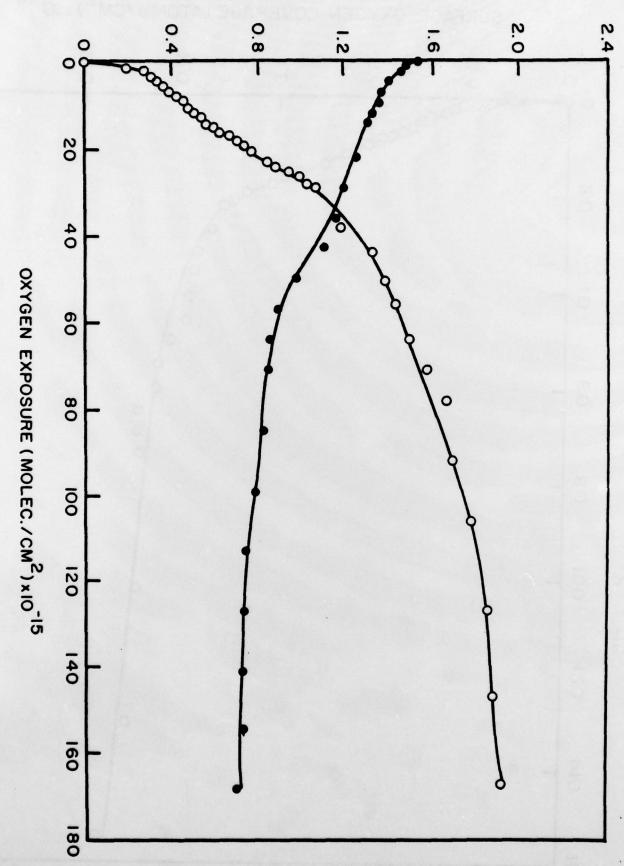
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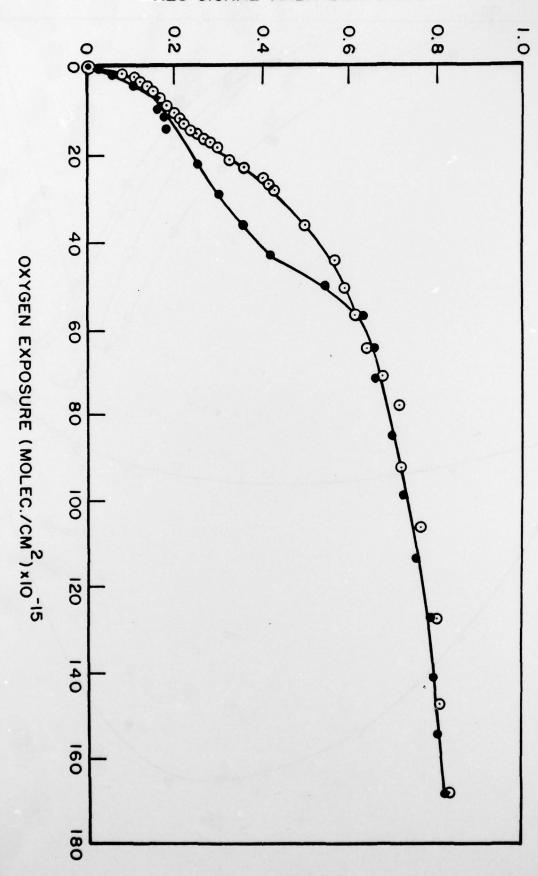
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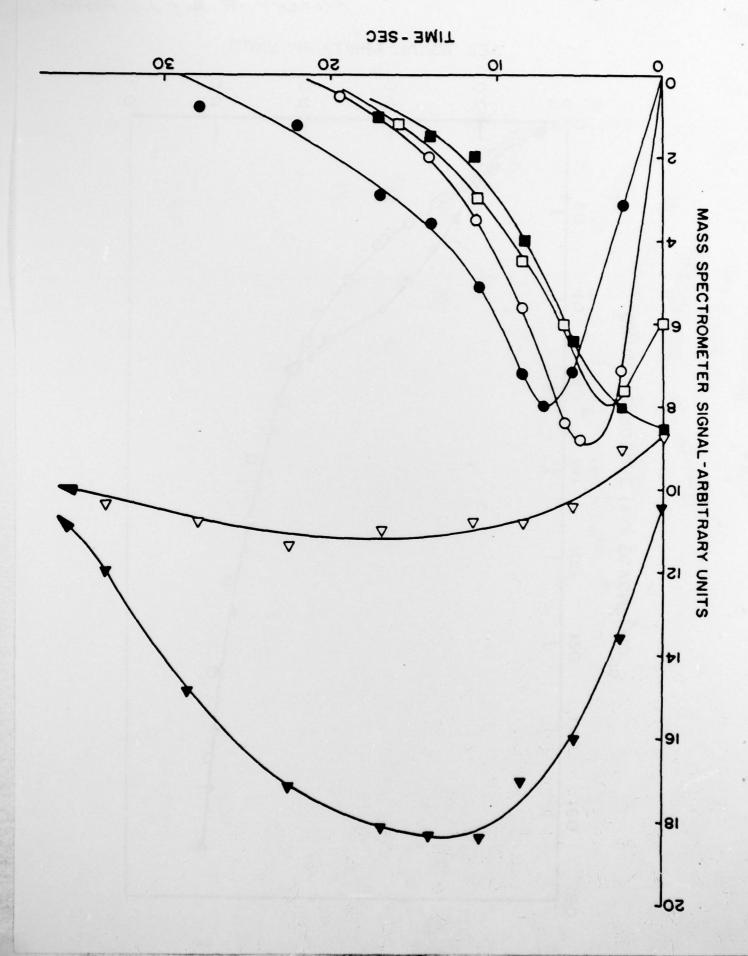


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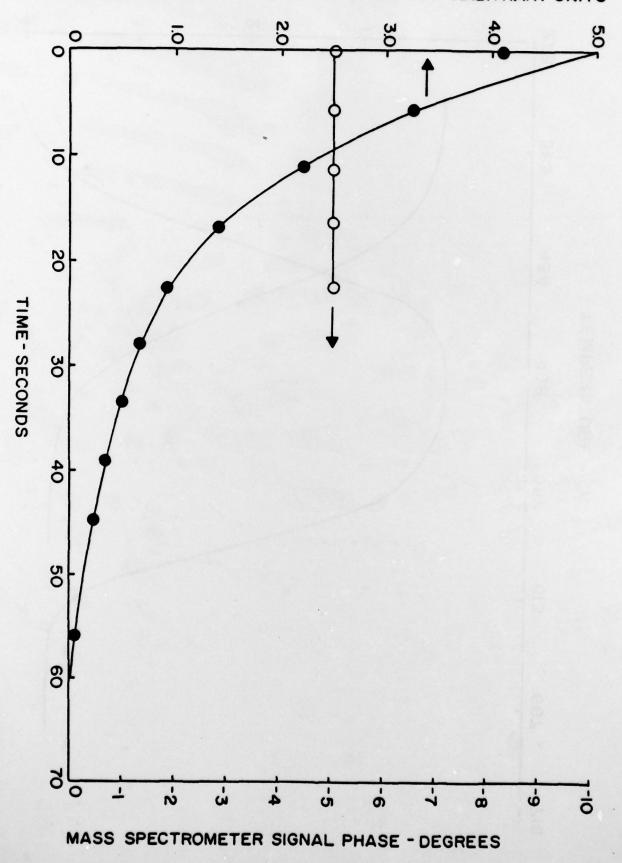


## AES SIGNAL -ARBITRARY UNITS

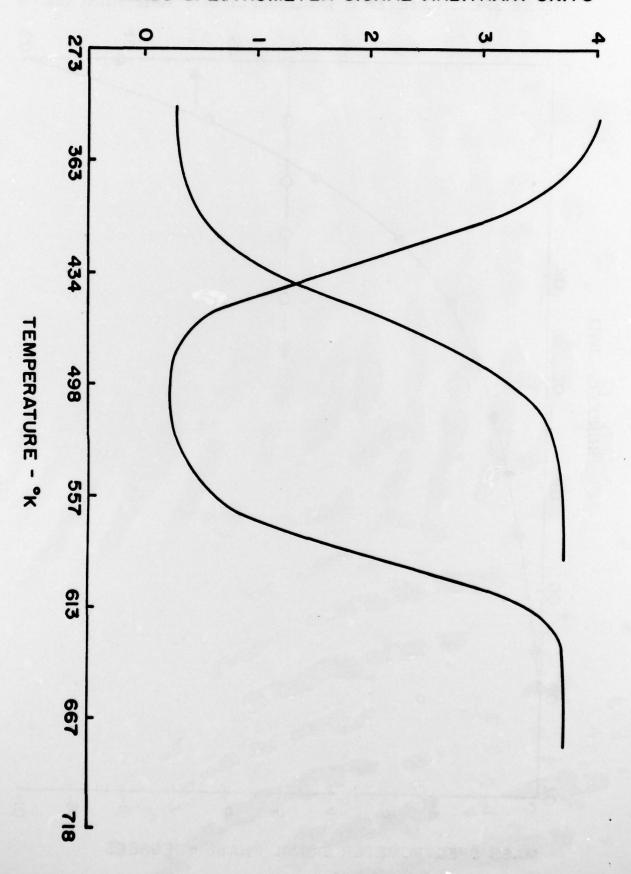




# MASS SPECTROMETER SIGNAL AMPLITUDE -ARBITRARY UNITS



# MASS SPECTROMETER SIGNAL-ARBITRARY UNITS



# SIGNAL AMPLITUDE - ARBITRARY UNITS

